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Comparative Evaluation of Oxygen Delignification Processes for Low and High Lignin Content Softwood Kraft Pulps

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Comparative Evaluation of Oxygen Delignification Processes for Low and High Lignin Content Softwood Kraft Pulps

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The present study explores the efficiency of delignification achieved during standard oxygen, double oxygen, and mini-oxygen [(E+O)$D_{kf=0.05}$(E+O)] delignification of high (kappa = 56.2) and low (kappa = 26.6) lignin content softwood (SW) kraft pulps in the context of the structural changes occurring in the lignin as measured by Nuclear Magnetic Resonance (NMR) spectroscopy. The relative bleachability of the high kappa pulps was determined to be superior to that of the lower kappa pulps during the oxygen bleaching experiments, whereas double oxygen (OO) runs in general were superior to single oxygen (O) runs. NMR spectroscopy demonstrated that part of the rationale for the higher levels of delignification in the high kappa pulps was a higher content of β-O-4 and methoxy lignin functional groups. In addition, the high kappa pulp possessed a lower number of resistant 5,5'-condensed lignin units and diphenylmethane structures. The NMR data also provided strong evidence for the

presence of para-hydroxyphenyl units, a relatively unique resistant structure whose elimination was approximately the same for both series of pulps. These new structures may potentially function as end capping termini that hinder access to bulk lignin, thus limiting the overall efficiency of oxygen delignification.

Keywords: ***Oxygen delignification, NMR Spectroscopy, Lignin***

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Introduction

The development of oxygen delignification (OD) systems arose in response to environmental concerns and impending EPA regulations on bleaching operations in the US pulp and paper industry. OD was intended to remove lignin from kraft pulp through application of high-pressure oxygen under alkaline conditions and offset downstream bleaching chemical requirements. This technology evolved as a mill-compatible operation that primarily offloads bleaching chemical demands, while simultaneously providing well-delignified pulp without compromising pulp physical properties. The pulp from the pulping operations, mainly consisting of carbohydrates (cellulose and various hemicelluloses) and a small lignin fraction (known as residual lignin, typically less than 5% by total mass), is subjected to relatively high-pressure oxygen conditions (range = 4-5 bar) under a hot (range = 90-105°C) alkaline environment from 30 to 90 minutes [Schroderus et al., 1997]. Unfortunately, despite process and chemical parameter modifications, the oxygen delignification operation cannot remove more than 35-50% of the residual lignin before sustaining detrimental oxidative carbohydrate degradation manifested as a loss in pulp CED viscosity and fiber strength [McDonough, 1996].

The loss in selectivity (change in overall lignin concentration/change in pulp viscosity) incurred during oxygen is cited as a major drawback to its continued implementation and therefore requires renewed efforts to provide the benefits of this environmentally benign technology. A theme in current OD research is to achieve a more fundamental understanding of the chemical factors governing delignification and carbohydrate damage. Research efforts by Gierer (1997), Gellerstedt (1987), Liu (2000), Moe (1998), Lucia (2000), Chen and Lucia (2001a), and Chen and Lucia (2001b) have investigated the fundamental nature of the reactions that occur in lignin during oxygen delignification. One of the insights obtained from these studies is the importance of several structural components

known as condensed and non-condensed phenolic structures (Figure 1) in delignification. The noncondensed phenolics appear to encourage delignification, whereas condensed phenolics tend to be more resistant. The basic chemical reactions that occur in delignification, however, do not change. For example, the typical oxidative reactions occurring during OD are shown in Figure 2. Nonetheless, many competing oxidative reactions occur during the process, modifying the chemical state of lignin in addition to promoting carbohydrate damage through radical intermediates such as hydroxy (generated as shown in Figure 2 in addition to diproportionation from organic peroxides).

The purpose of the present effort was to define the relative bleachability of high and low lignin content pulps as a function of the OD system employed and specific conditions and provide a fundamental basis for the results observed through the use of ^{13}C and ^{31}P NMR spectroscopy.

Experimental Section

Materials. All chemicals and reagents were commercially purchased from Aldrich, Fischer, or EM Science and used as received, except for the ACS-grade *p*-dioxane which was refluxed for one hour over sodium borohydride and distilled. In-house distilled water was used for the oxygen delignification studies. The low kappa (LK) kraft SW pulp was generously supplied by a member company of the Institute of Paper Science and Technology, whereas the high kappa (HK) kraft softwood (SW) pulp was manufactured in-house by controlling the H-factor (time/temperature cooking profile) in a kraft batch cook.

Oxygen Delignification Trials and Chlorine Dioxide Bleaching. The metal contents (iron, copper, magnesium, and manganese) of the brownstock starting pulps were determined using ICP to

qualitatively assess the effect of nonprocess elements in the reactions. All OD experiments were conducted in a pressurized reactor bomb under controlled mixing that was temperature controlled. A sample trial is described as follows: a pulp was added to a preheated solution of water at a selected temperature containing a concentration of 2.5% and 0.1% concentration of NaOH and $MgSO_4$, respectively, relative to dry pulp mass. The amount of water for the experiments was generally added in a 9:1 m/m ratio to pulp (10% pulp consistency). After the pulp equilibrated to temperature (typically 5-10 minutes), a constant pressure of 90 psi was applied and the reaction "clock" was begun and allowed to run up to 60 minutes. Afterwards, the reaction was stopped by removing the pulps from the reactor and isolating the straw-colored effluents through a Whatman #4 filter paper. The pulps were thoroughly washed with excess distilled water until the filtrate was clear. They were allowed to air dry or used in a subsequent oxygen delignification trial with or without effluent from the prior run (carryover). All pulps were tested for lignin content using TAPPI test method T256c and CED viscosity using TAPPI test method T258c. Fresh solutions of chlorine dioxide were prepared before use and applied to the pulps as either a 0.05 or 0.20 kappa factor (no. equivalents of chlorine multiple/kappa number of pulp; 1 equivalent ClO_2 = 2.63 equivalents Cl_2) in a Kapak polyethylene bag. ClO_2 bleaches were conducted at 10% consistency and 70°C for 30 minutes.

Residual Lignin and Effluent Lignin Isolation. The pulps were acetone extracted in a Söxhlet extractor for 24 hours, thoroughly washed with water, and air dried before proceeding to isolate the residual lignin. The air-dried pulp was placed in a three-necked round-bottom flask and diluted with a 9:1 v/v of *p*-dioxane and 0.10 N HCl to yield a final consistency of 4%. The pulp slurry was refluxed for 2 hours under argon positive pressure and subsequently allowed to cool to room temperature. The slurry was filtered to remove the hydrolyzed pulp and worked up according to Gellerstedt's (1991) established procedures. Yields for the lignin isolation ranged from 45 to 55% based on original lignin

content of the pulp. Effluent lignin from the trials was isolated by concentrating the effluent (50% reduction in volume) and acidulating it with 1 N HCl until the pH was 2.0. The precipitated lignin was frozen to coalesce low molecular weight fragments, thawed, and centrifuged to yield a thick, brown paste. The paste was rinsed with pH = 2.0 water, centrifuged, and collected. This latter process was repeated twice. All of the subsequent lignin fractions were collected into one flask, freeze-dried, and oven dried at 40°C overnight.

NMR Spectroscopy. All nuclear magnetic resonance (NMR) spectra were collected on a Bruker DMX 400 MHz NMR spectrometer.

^{13}C NMR Spectroscopy. ^{13}C NMR spectra were obtained under quantitative conditions through the use of an inverse-gated pulse sequence with a $\pi/2$ pulse, a sweep width of 330 ppms, and a 10-second delay. In general, 100-200 mg of lignin/mL was dissolved into 0.4 mL of d^6-DMSO (dimethylsulfoxide) and heated to 50°C. All output signals were Fourier transformed using 10-Hz line-broadening and analyzed using reported chemical shifts for lignin functional groups [Nimz et al., 1982]. All integrations were calculated relative to an integration value of 6 carbons assigned for the aromatic functionalities [Robert, 1992]. The accuracy of this method is typically within 5% which was confirmed by our experiments.

^{31}P NMR Spectroscopy. Lignin isolates were phosphitylated with 2-chloro-4,4-5,5-tetramethyl-1,3,2-dioxaphospholane following the procedure of Granata and Argyropoulos (1995) and subsequently analyzed by ^{31}P NMR. All standard deviations are < 5%.

Results and Discussion

Pulp Chemical Response to Oxygen Delignification Trials. A series of kraft SW pulps that were high and low in lignin concentration were subjected to controlled OD experiments. All subsequent analyses were done on the basis of the physical characteristics of the pulps and the conditions used for OD. One of the important physical characterizations, profiling of metal profiles in the pulps, was obtained using ICP since metals have been shown to exert an influence on the chemistry during OD [Soini et al., 1997]. The values obtained were within reasonable limits for these pulps [Werner et al., 1999] and are shown in Table 1.

The conditions used for the experiments in this study are shown in Table 2. Pulp/water ratios (consistency, 10%) and added magnesium sulfate concentration (0.1% relative to dried pulp or 1000 ppms) were maintained constant, while the specific conditions for single oxygen (O), double oxygen (OO), and mini-oxygen ((E+O)D(E+O)) trials are shown in Table 2.

Past research efforts have indicated that higher lignin content (high kappa) pulps possess increased bleachability (change in lignin concentration/charge of NaOH) than their lower kappa counterparts [Moe et al., 1999]. The phenomenon observed was not ascribed to leaching effects as described by MacLeod (1996) or Donnan equilibrium effects arising from metals. The increased bleachability of the higher lignin content pulp was due in part to the reactive nature of the lignin and its environment. Past studies have shown that the environmental levels of magnesium in pulp exert a beneficial influence on the progress of the selectivity of the delignification over carbohydrate degradation [Liden and Ohman, 1997; Brown and Dawe, 1996]. This may be due to their ability to sequester redox active metals (such as iron and manganese) that function to produce radicals from the hydrogen peroxide produced during an oxygen delignification process (see Figure 2). The higher

kappa pulp is enriched in magnesium by a factor of over two to one versus the levels in the LK pulp, a level which is statistically significant for observing differences in the delignification process considering that many mills run at levels of added magnesium around 1000 ppm. Another advantage that the higher kappa pulp has is its inherently low iron level by a factor of almost four. This would serve to hinder the overall metal-induced redox activity occurring during OD and would reduce the consumption of in situ hydrogen peroxide.

The lignin concentration of the two sets of pulps was obtained after each set of OD trials. The OO set of experiments achieved the best delignification compared to all the other OD experiments. As shown in Figure 3, the reductions in the lignin for the LK pulp were most pronounced for the OO set of experiments at all NaOH (caustic) charges. For the LK pulp, the delignification appeared to level off at the 2.5% middle caustic charge, whereas the HK pulp continued to delignify by almost 50% between the middle 4.1% and high 5.8% caustic levels. Clearly, OO was the superior oxygen delignification technology for the HK pulp. The O set of experiments also behaved in a manner similar to the OO, whereas the mini-O (see Table 2 for details on mini-O conditions) compared favorably in the LK case, but was not nearly as efficient in the HK case. The ability of the mini-O to perform so well in the LK case may be a function of the interstage chlorine dioxide treatment activating the pulp lignin to subsequent oxygen reactions [Lucia et al., 2000]. The level of condensed phenolics in the lignin appears to be diminished somewhat from past studies. What is also surprising about the LK delignification studies is the remarkable similarity of the final kappa numbers observed between OO and O trials. An OO stage for these samples is not nearly as efficient as demonstrated in the HK case. This suggests that the nature of the residual lignin is not as responsive to a temperature/oxygen profiling system, indicating that an O for an LK pulp performs in a satisfactory manner.

The OO case demonstrates much more delignification response in the HK pulps over the LK pulps (almost 50%) than observed in the single O stage. This result is consistent with the general trends obtained from the patented OxyTrac™ process that defined the optimal set of conditions for maximum oxygen delignification [Bokström and Kobayashi, 2000]. The first stage initiates the chemical reactions that account for delignification under high oxygen concentrations and mild heating conditions, whereas the second stage is essentially a lignin extraction stage done under high temperature. The variation in delignification between the lower and higher kappa pulps may be attributed to the abundance of easily degradable lignin structures in the higher kappa pulps as shown in the subsequent NMR analyses.

The pulp bleachability was plotted for both sets of pulps and is shown in Figure 4. Pulp bleachability gauges the ease associated with removing lignin from pulp. Again, as alluded to previously, the results show that the HK pulp has a better delignification response than the LK pulp. In fact, an O for the LK system appears to approach the bleachability of an OO for the HK system, again indicating the ability of the O to perform efficiently for the LK pulps.

The integrity of the pulp as given by average molecular weight or the observable known as CED viscosity (measures the chain length of the cellulose polymer) cannot be compromised or else the physical nature of the pulp will be degraded. The changes observed in the viscosities for the pulps under the various oxygen delignification processes in this study are displayed in Figure 5. The OO sequence was very favorable for the pulp viscosities of both the lower and higher kappa pulps. In the lower kappa pulp, the OO sequence provided more delignification than either O or (E+O) and provided almost comparable viscosity retention versus the mini-O. The delignification and viscosity efficacy of the OO in the lower kappa pulp case validates the OxyTrac™ process (vide infra). Also, an O, despite providing comparable delignification to OO, did not perform as satisfactorily as OO nor

mini-O in retaining viscosity. This latter result strongly implies that a single O stage is not being satisfactorily used in current industrial applications. In essence, the bulk of the "useful" delignification reactions are occurring early in the reaction scheme, and forcing the same conditions over the timescale induces carbohydrate damage. The brunt of the oxygen delignification may have been completed as shown in the first part of the OO, where the second phase behaves as an extraction stage for the degraded lignin that diffuses from the pulp. The mini-O appears to be too mild an extreme to significantly induce delignification, but serves to demonstrate the level of viscosity retention that can be expected. Certainly, OO is on par with the mini-O in viscosity retention, but has sufficiently aggressive delignifying conditions for optimal delignification, but less so than the O.

The HK pulp, alternatively, demonstrates that a mini-O has much better viscosity retention than either an O or OO, but performs less efficiently with respect to delignification. Figure 6 illustrates the selectivity (change in kappa/change in viscosity) of the oxygen delignification systems for all of the pulps. Despite the superior viscosity retention of the mini-Os, the OO sequences clearly have the superior selectivity coefficients mainly because of their superior delignification ability. This enhancement in selectivity is directly attributable to the profiling of the pulp system by the OO technology that maximizes lignin fragmentation and minimizes carbohydrate damage. An O stage is probably too aggressive for maximum selectivity since lignin leaching is likely a critical component of an OD process. If the lignin leaching is not allowed to occur, the more resistant (e.g., condensed phenolics) structures may not be attacked as easily as the carbohydrates under typical O conditions.

Significance of Condensed Structures in the Oxygen Delignification Response. Lignin structural characterizations have been used to provide an underlying explanation for the selectivity and the levels of delignification. The HK pulps exhibited an increased level of delignification as compared to the lower kappa pulps and this could be partially explained by both the carbon (^{13}C) and

phosphorus (^{31}P) NMR techniques. ^{13}C NMR spectroscopy is a tool that has received considerable attention in the NMR literature to identify structural features that influence delignification [Newman et al., 1993]. This technique provided a very useful way to rapidly analyze the variety of functional groups in the lignin, and the results are shown in Table 3. The structural differences in the residual lignin between the two pulps are consistent with previous investigations of residual lignin from pulps of varying kappa numbers [Froass et al., 1996b]. It was found from these studies that higher kappa pulps (40-50) possessing a higher concentration of methoxyl groups tended to be easier to delignify. The result is based on the oxidative alkaline reaction of methoxyl which forms formaldehyde as was discussed by Gierer (1970). In addition, the higher levels of β-O-4 groups in the HK lignin provide a more reactive site for soda reactions that expose more phenolic groups for oxygen delignification (as shown in Figure 2a).

Conversely, a potential basis for the resistance of the LK pulp to delignification is from the presence of the diphenylmethane (DPM) structures (see Figure 1) and the ratio of aromatic C-R (PhC-R) to aromatic C-H (PhC-H) units. The lower kappa pulp has threefold more DPM structures as compared to the HK pulp. The DPM phenolic structures have warranted much attention as likely contributors to the inactivity of lignin during oxygen delignification due to their robustness in model studies [Xu et al., 1995]. In fact, they are a typical example of "condensed" aromatic structures, structures that have been implicated as likely oxidatively resistant lignin structures [Argyropoulos and Liu, 2000]. The increasing PhC-R/PhC-H ratio in the lower kappa pulp also indicates an increasing level of condensed phenolic structures. Independent ^{31}P NMR studies demonstrated that the condensed/noncondensed ratios were 1.15 and 1.07 for the lower and high kappa pulp residual lignins, respectively, which support the ^{13}C NMR results.

The oxidative chemistry that occurs at the phenolic sites is of great importance since these sites represent the primary reactive sites during oxygen and chlorine dioxide reactions [Froass et al., 1996b]. The phenolic changes for representative cases (low and high caustic charges are displayed) from the original pulp to the effluent are shown in Figures 7 and 8 for the LK and HK pulps, respectively. These analyses provide a direct, efficient, and quantitative way of investigating the chemical changes occurring in the pulp through investigating the structural units that are eliminated. In almost all cases, the depletion of the noncondensed phenolic units is greater than the condensed phenolic structures. In the mini-O case, however, the relative difference in magnitude between the depletion of the noncondensed versus the condensed is not as exaggerated, a difference that can be attributed to the interstage ClO_2 treatment, which aids in removing both condensed and noncondensed phenolic structures with almost equal facility [Lucia et al., 2000].

The 2:1 ratio of noncondensed to condensed lignin structure removal for the HK pulp case versus the LK pulp is unusual considering that both native pulp lignins have roughly equal amounts, within 10%, of these functionalities. The noncondensed structures of the HK pulp are predisposed to easier delignification potentially because of the almost 20% higher levels of β-O-4 linkages in the noncondensed structures that have been previously determined to be consistent with increased bleachability. The lower levels of condensed structures in the HK effluent lignin are therefore likely associated with the relatively greater ease of the noncondensed structure removal during delignification. The OO low charge for the LK provided interesting results. It was found that the effluent lignins displayed an enrichment in condensed phenolics as compared to the other trials. This result is supported by the increased selectivity obtained as well as the high level of aliphatic hydroxyl groups and para-hydroxy phenyls in the effluent as compared to the other samples. It appears that the

OO trial provides significant chemical changes that improve the ability of the trial to delignify selectively.

Analysis of Carboxylic Acid Content. Another approach to evaluating the impact of lignin on delignification is through analysis of the oxidized lignin fragments recovered after delignification. These fragments reflect the state of the lignin after oxidation chemistry has occurred and give insight into the structural components that are necessary for lignin diffusion/leaching. The recovered lignin fragments (from acid precipitation of the effluent liquor) were analyzed by quantitative ^{31}P NMR spectroscopy and the results are shown in Figure 9. The acid group content in general of the effluents was increased by a factor of 2-4 with respect to the original residual lignin acid group content. This result is consistent with the general oxygen chemistry that occurs to obtain a soluble form of lignin. Figure 1 demonstrates that an increase in the muconic and methyl ester structures derived from lignin occur via oxygen radical reactions which lead to products that are more soluble than the residual lignin. The residual lignins of the LK and HK pulps have an acid content of approximately 0.25 mmol/g lignin that corresponds to what has been previously reported for similarly generated kraft pulps [Froass, 1996a]. In the LK pulps, it is not surprising to find that the OO-high caustic charge provides the greatest amount of acid-modified effluent lignins. This corresponds to the highest extent of delignification as shown in Figure 3. Surprisingly, although an O-high caustic charge provides an equivalent level of delignification, the level of acids found is not nearly as great as found in a OO. Past studies have shown that the level of oxidation that occurs during a high caustic single stage oxygen delignification of a typical LK kraft pulp (kappa 20-30) is very high [Argyropoulos et al., 2000]. The molecular weight of these fragments is extremely small (<< 1000 D) and almost impossible to quantitatively recover. It was found that attempts to derivative these samples using acetylation for GPC analysis did not work, strongly suggesting that the level of oxidation is very high

and requires esterification for analysis. Remarkably, the HK pulps were similar in acid response, except for the OO stages. It is clear that the chemistry that leads to delignification between the high and low kappa pulps is not similar. Although the levels of delignification between the low and high kappa pulps were similar, the extent of oxidation found in the HK effluent lignins was much less. This strongly suggests that the lignin in the HK pulps did not require as much oxidation to cause removal, a finding that attests to the lability of the lignin in the HK pulps. High kappa pulps are known to exhibit a higher delignification response or increased bleachability as shown in Figure 4 [Steffes et al., 1998; Andtbacka, 1986]. This increased bleachability has tremendous advantages for higher delignification selectivity responses. The additional chemical factors that point to the higher bleachability response of HK pulps are the reduced quantity of condensed lignin structures that therefore require less oxidative chemistry for removal (vide infra) and the differences in the character of the oxidative chemistry occurring on the lignin itself as related to, for example, the aliphatic hydroxy groups.

Aliphatic Hydroxy Group Changes. Quantitative changes that occur on the aliphatic hydroxy group generally signify a degradation of the macromolecular lignin structure [Froass, 1996; Sun and Argyropoulos, 1995]. The aliphatic hydroxy content of lignin mostly consists of primary and secondary hydroxyl groups located on the C^{γ} and C^{α} of the phenylpropane side chain of lignin (See Figure 1). As shown in Figure 10, in almost all of the trials, it was found that the HK lignins were enriched in aliphatic hydroxyls over the LK lignins. This result may indicate that the oxidative chemistry that causes the delignification in HK pulps occurs through the side chain, perhaps because of the naturally higher levels of aliphatic hydroxyls in HK over LK by over 10%. The OO-low charge for LK appears to have a profound effect on the chemistry of delignification as evidenced by the changes in the phenolics, aliphatic hydroxyls, para-hydroxyphenyls (see below), and selectivity. The

effluent lignin from the OO-low charge for LK enriches the aliphatic hydroxyls content more than expected. This result seems to provide support for the finding of the strong enrichment in condensed phenolics during this stage as well as the para-hydroxy phenyls, a newly implicated resistant group. These latter findings are well supported by the increased selectivity evidenced during this stage that is competitive even with the HK pulps.

Implication of Novel Resistant Phenolic Structures for Delignification. One of the more remarkable achievements of this investigation was substantiating the existence and importance of para-hydroxyphenyl groups in the delignification process. Recently, there have been several noteworthy efforts that have described the presence of these structures in bleaching chemistry [Poppius-Levlin et al., 1999; Tamminen et al., 1998; Akim et al., 2001]. In this report, we provide one of the first reports for their involvement and role in the oxygen delignification process (shown in Figure 1). These structures have been implicated to be resistant to degradation reactions that lead to soluble byproducts. The amount of these structures that was found in our brownstock samples (measured over the range of 138.3 ppm to 137.0 ppm) was approximately 0.10 mmol/g lignin. The enrichment in the effluent lignin samples averaged approximately 10%. As shown in Figure 11, this enrichment in the effluent lignins is quite small, but several of the changes can be correlated to the macroscopic findings in this study. For example, the OO stage has demonstrated tremendously high delignification selectivity and high delignification levels, which is attested by the data in Figure 11. The enrichment in the groups for the LK pulp was especially large in comparison to the rest of the lignins. In fact, even the HK pulp demonstrated a slightly higher enrichment in this level among its competing oxygen delignification trials. Yet, in general, removal of this group was low, owing to its rather robust chemical inertness. This result strongly suggests that the native structures are robust and not as susceptible to the normal oxidative pathways available to groups more prone to degradation,

such as the noncondensed phenolics. The possibility that these structures act as end capping units and hinder the further oxidation of lignin is likely and an issue for further exploration. They may be located at termini that prevent accessibility to the portions of lignin that are oxidatively degraded. In an independent series of experiments, we added phenol to several oxygen delignification reactions with and without typical LK kraft pulp and found from GC analysis virtually complete recovery (> 99%) of the phenol. This new structural unit in lignin may be significant in the overall scheme of oxygen delignification efficiency and opens the door to its potential as a delignification stopping unit in oxygen delignification systems.

Conclusions

The current study has provided an overview of the results of various oxygen delignification trials with the objective of comparing their overall delignification efficiency and providing a spectroscopic justification for the results obtained. The studies confirm the hypothesized benefits of a double oxygen (OO) stage for both higher and lower kappa pulps. Not only is the system able to provide enhanced delignification, but also it maintains the integrity of the pulp. The basis for the increased benefits of an OO stage in the HK stems from the more labile nature of the lignin that may arise from the higher concentration of β-O-4 linkages in the lignin matrix, reduced amount of condensed structures, DPMs, and higher methoxyl content. The differences in the higher levels of Mg and lower levels of Fe in the HK pulp may account for part of the increased selectivity. An OO for the LK pulp at low caustic charge appears to be most promising for LK pulps. The chemistry that arises in this system appears to target the aliphatic hydroxyls, improve removal of condensed phenolics, and provide greater removal of the para-hydroxy phenyls. The mini-O system continues to

be a promising technology to remove lignin while keeping a very high viscosity. Analysis of the residual lignin and all of the effluent lignins emphasized the role that condensed and noncondensed phenolics play in controlling oxygen delignification. A mini-O stage is encouraging because the interstage D attacks the condensed phenolics very efficiently, while concomitantly optimizing the performance of a subsequent (E+O) stage. One of the important developments during the work was the existence of the para-hydroxyphenyl units that are in general robust during oxygen delignification although OO systems appear to impart greater changes to them. Future developments and advances in oxygen delignification technologies will involve a better understanding of their role in controlling the extent of delignification.

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Table 1. Metal Analysis (ICP) of the Kraft SW Pulps

Metal	Low Kappa SW Pulp (ppm)	High Kappa SW Pulp (ppm)
Na	720	884
K	359	88
Mg	315	727
Ca	2590	1990
Mn	33	57
Fe	70	18
Ni	1	1

Table 2. Relevant Oxygen Delignification Conditions Employed for all of the Experiments[a]

Stage	O_2 Pressure, psi	NaOH[b], % low kappa, high kappa	Temp., °C	Time, min.
O	80	1.5, 2.5, 3.5, 2.5, 4.1, 5.8	105	80
OO	i) 130 ii) 60	1.5, 2.5, 3.5, 2.5, 4.1, 5.8	i) 80 ii) 105	i) 20 ii) 60
$(E+O)D_{kf=0.05}(E+O)$[c]	80	1.5, 2.5, 3.5, 2.5, 4.1, 5.8	i) 80 ii) 70 iii) 80	i) 20 ii) 30 iii) 20

[a]$MgSO_4$ charge was 0.30%; consistency was 12%; [b]the low kappa pulp was 26.6 and high was 56.2. Low charge refers to 1.5 and 4.1 for the low and high kappa pulps, respectively, whereas middle and high charges, likewise refer to the corresponding caustic charges between the low and high kappa pulps; [c]caustic charge was split between two (E+O) stages in which the pulp was washed between stages and treated with a 0.05 kappa factor of ClO_2 (D), at 10% consistency, 70°C for 30 minutes, giving a terminal pH of 2.2.

Table 3. Functional Group Analysis by ^{13}C NMR[a]

Stage	High Kappa	Lower Kappa
CH_2-Phenyl (DPM)	0.03	0.09
MeO-Phenyl (methoxy)	0.89	0.81
Cβ in ββ and Cβ in β	0.14	0.13
Cγ in β-O-4	0.32	0.27
Aromatic C-R/Aromatic C-H	1.96/1.00	2.05/1.00
Acid (COOHs)	0.17	0.31

[a]All integration values were normalized against an assigned value of 6 for the aromatic carbon integration value

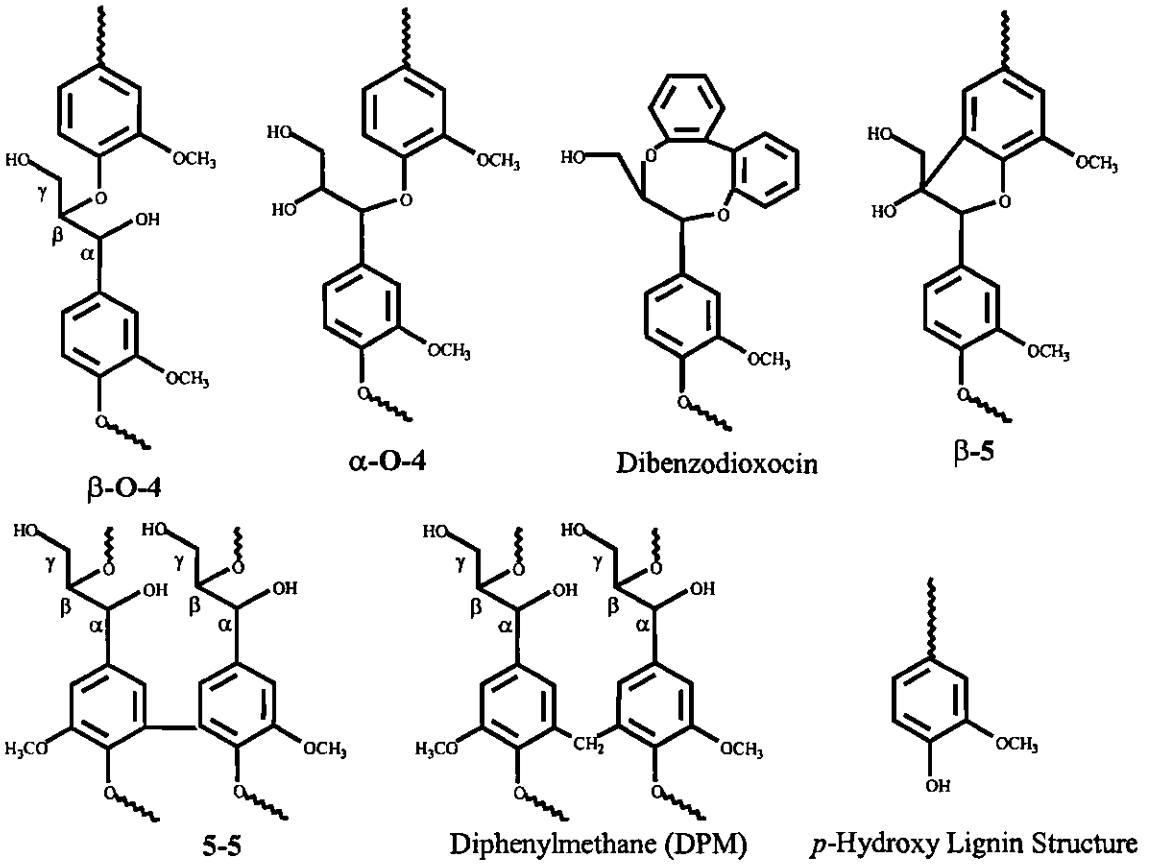
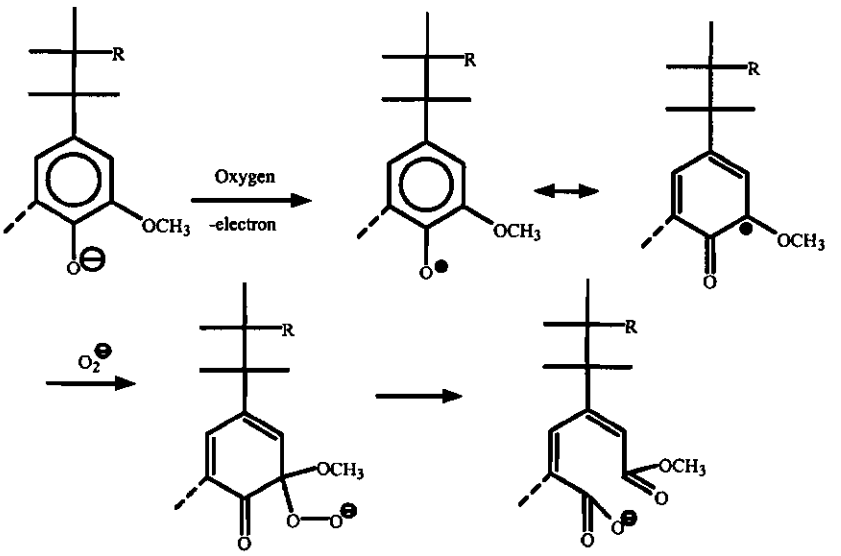
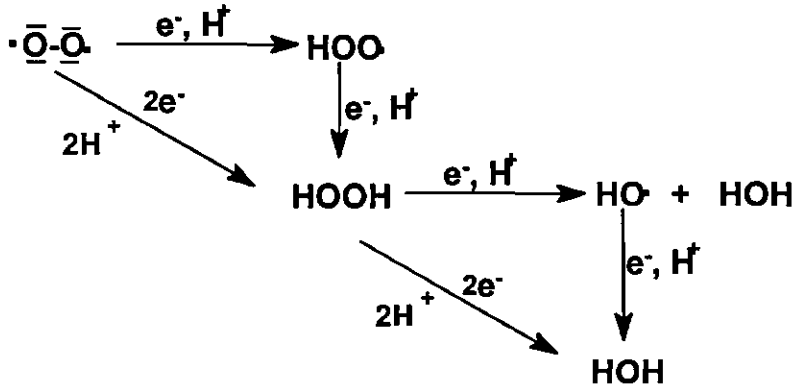


Figure 1. Interunit linkages that are typically found in softwood kraft lignin. Structures such as β-O-4 are referred to as noncondensed structures, whereas 5-5 and diphenylmethane are condensed structures.



(a)



(b)

Figure 2. The relevant oxidation reactions occurring during oxygen delignification are shown. Part **(a)** illustrates the oxidation of a canonical lignin structure to muconic acid and methyl ester derivative whereas **(b)** illustrates the 4 electron reduction process where dioxygen is transformed to water.

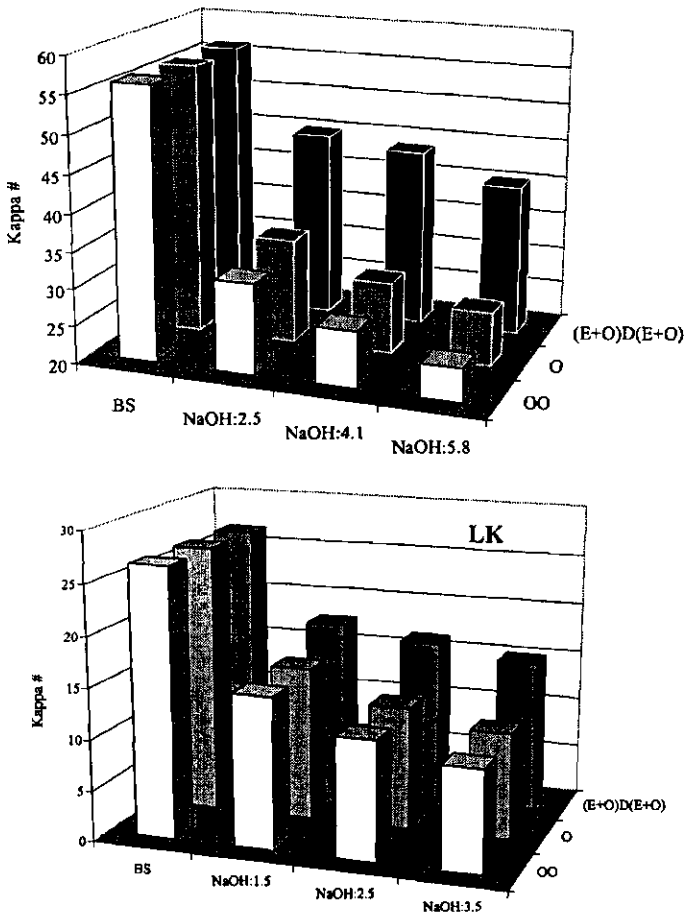


Figure 3. The measured kappa numbers for all the various oxygen delignification trials (lower kappa on left and higher kappa on right) as a function of NaOH concentration (%) versus dry weight of pulp

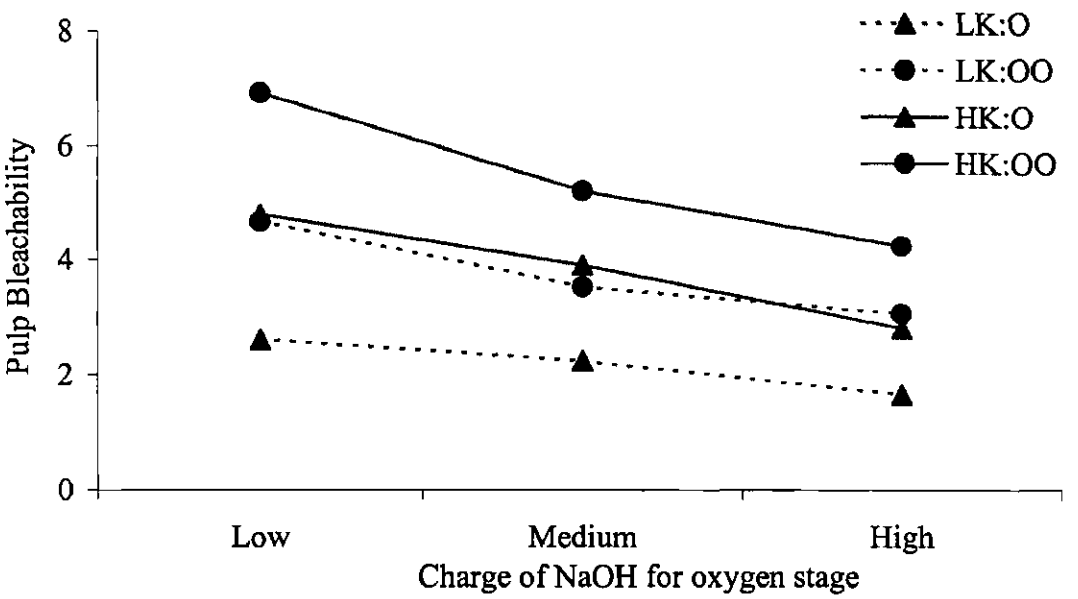


Figure 4. The pulp bleachability (caustic charge consumed/drop in kappa number) of the low kappa pulp (LK) and the high kappa pulp (HK) for O and OO trials.

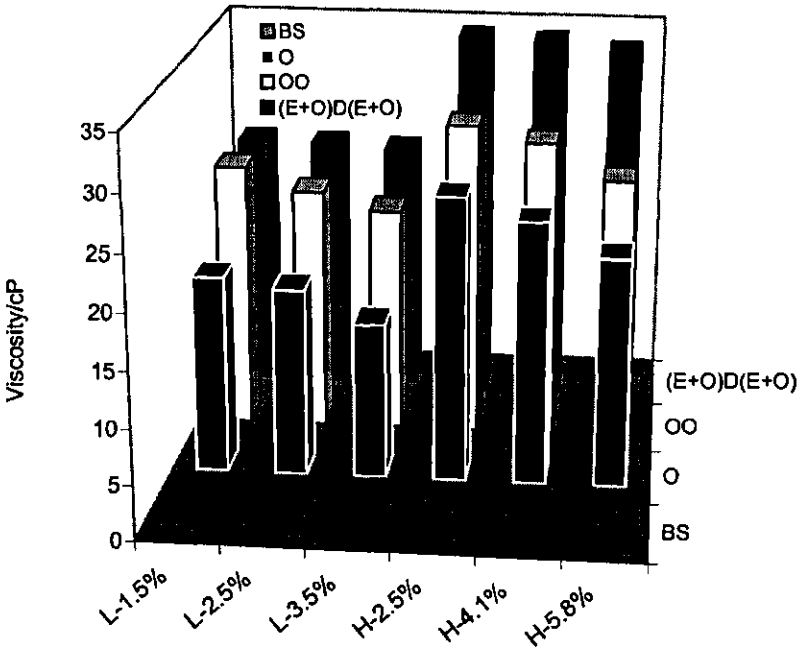


Figure 5. The viscosities of the low and high kappa pulps as a function of base concentration.

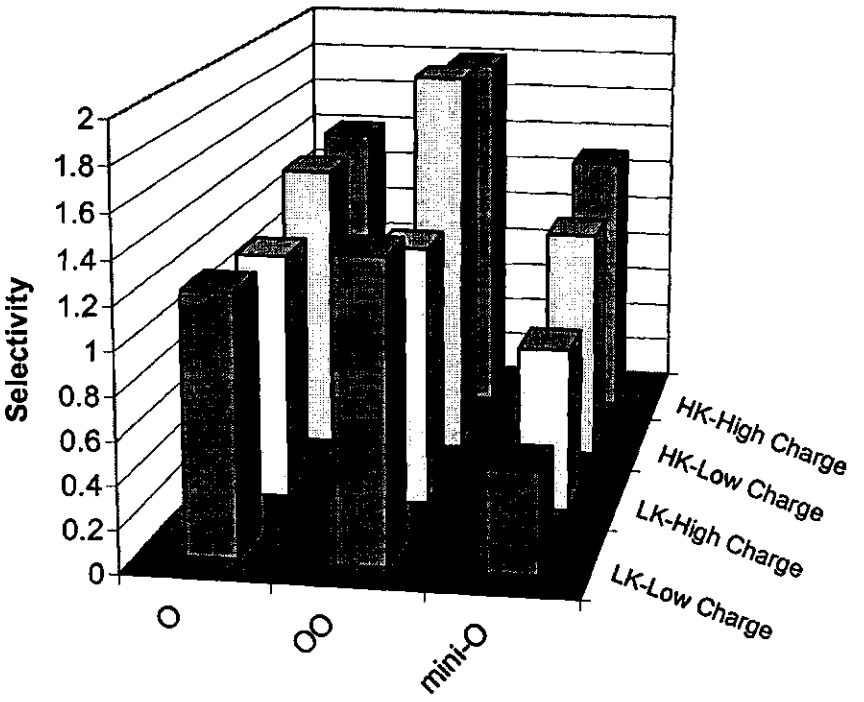


Figure 6. The selectivity (change in lignin content/change in viscosity) of the pulps from the oxygen delignification trials obtained (HK = high kappa, LK = low kappa, whereas the charge refers to low (1.5% and 2.5% for LK and HK, respectively) and high (3.5% and 5.8 % for LK and HK, respectively) applications of NaOH on dry pulp.

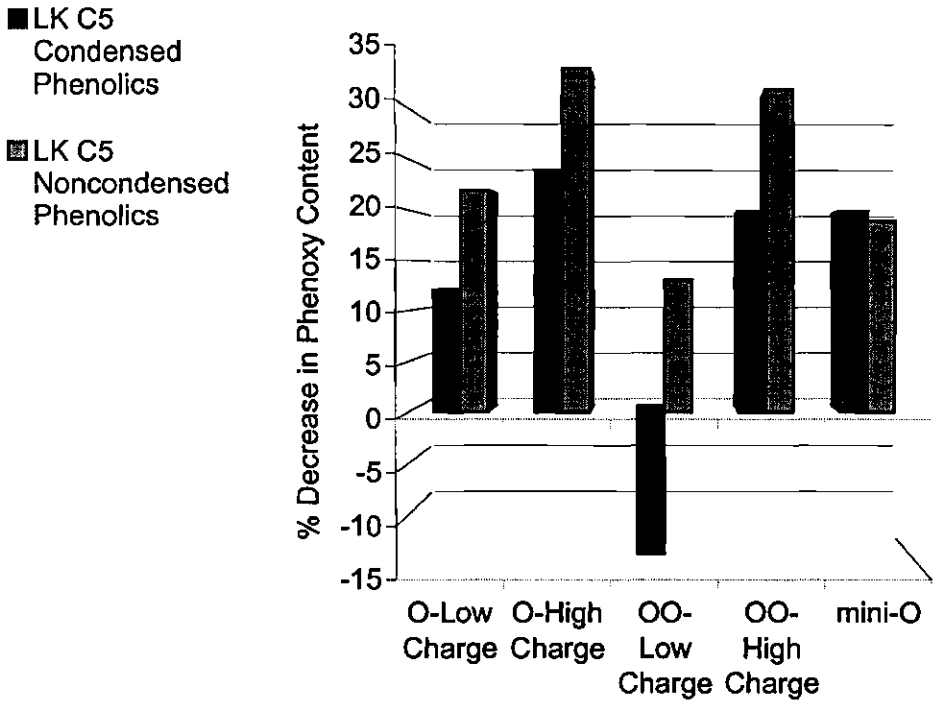


Figure 7. Changes in the residual lignin phenoxy content as determined from the recovered effluent lignins of the low kappa pulps after O, OO, and mini-O trials. The low kappa brownstock had C5 noncondensed and C5 condensed concentrations of 0.84 and 0.73 mmol/g of lignin, respectively.

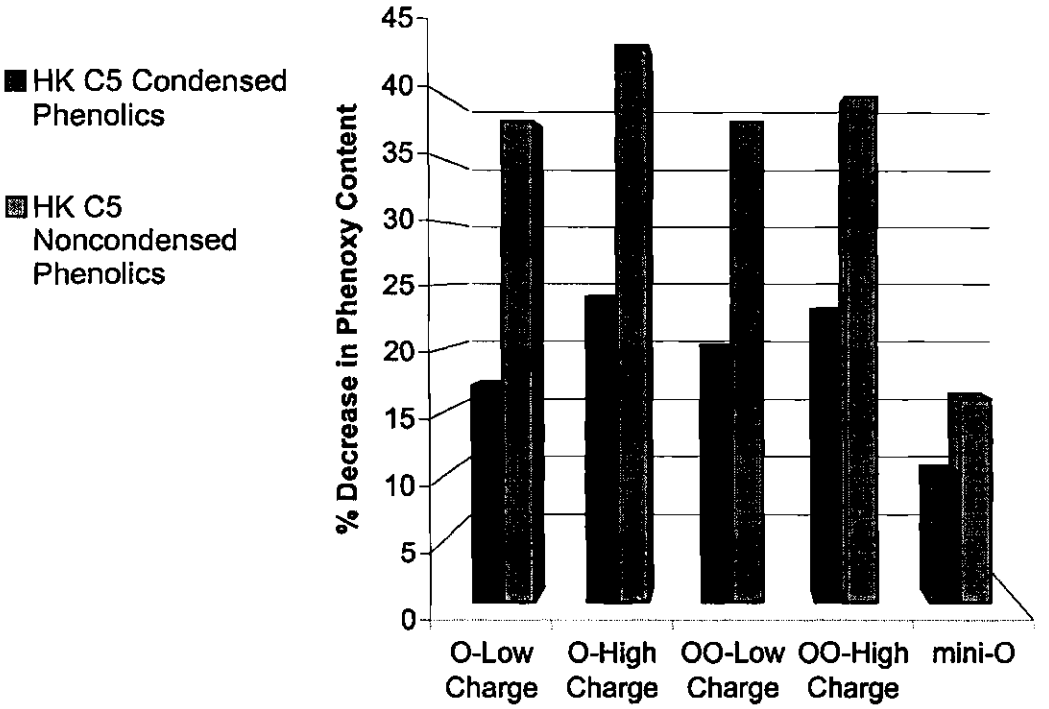


Figure 8. Changes in the residual lignin phenoxy content as determined from the recovered effluent lignins of the high kappa pulps after O, OO, and mini-O trials. The high kappa brownstock had C5 noncondensed and C5 condensed of 0.88 and 0.82 mmol/g lignin, respectively.

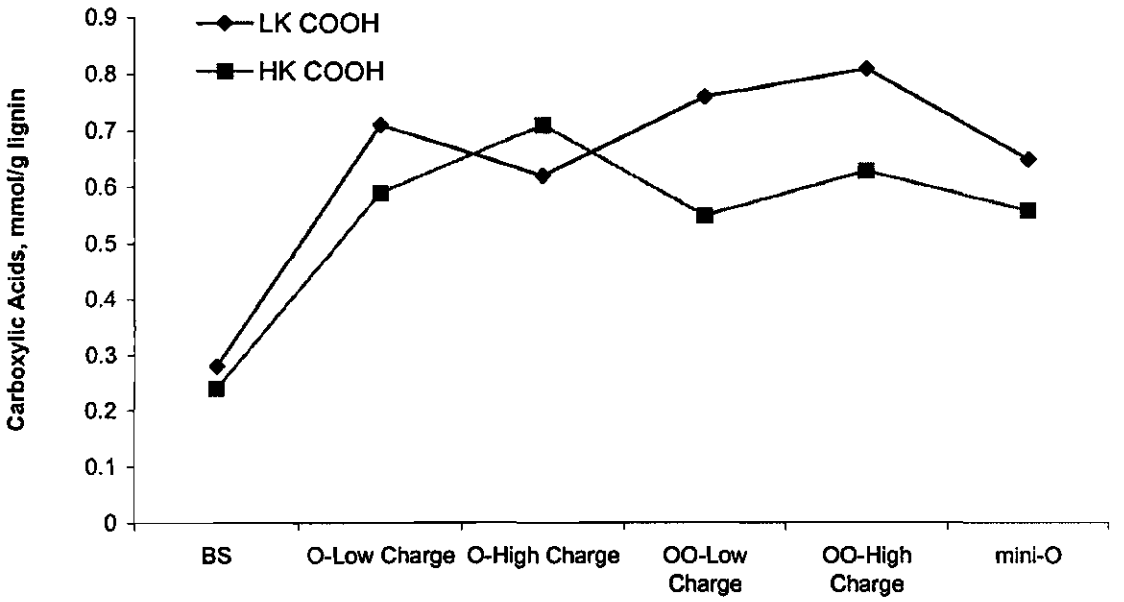


Figure 9. The quantitative concentration of carboxylic acids determined in the pulp lignin effluents that were obtained from the O, OO, and mini-O trials of the LK and HK pulps.

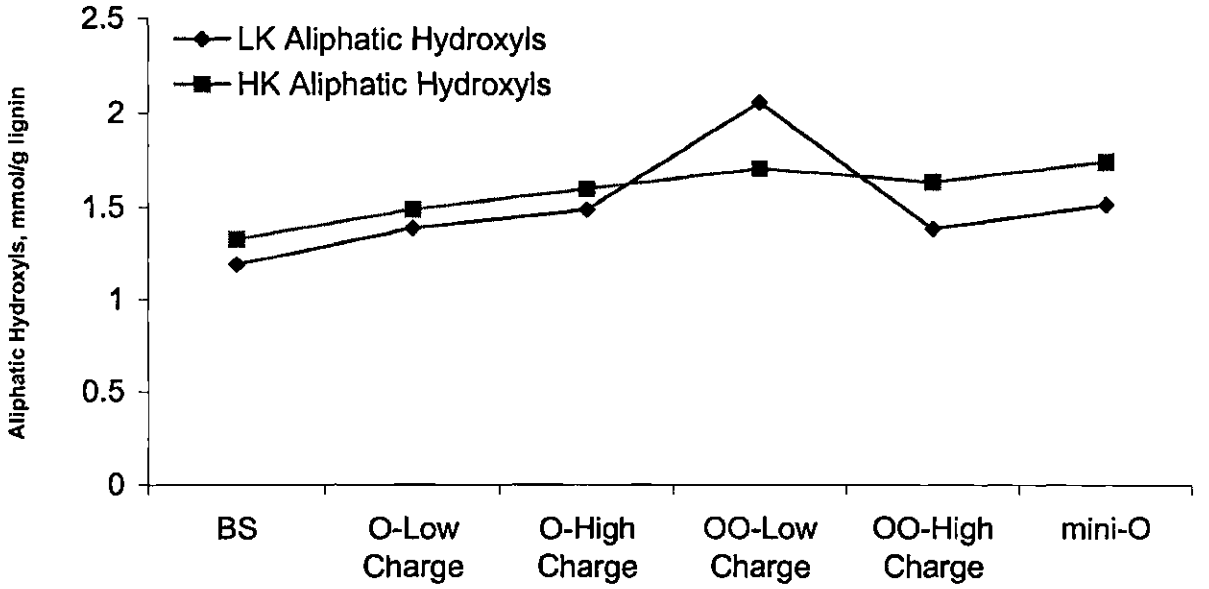


Figure 10. The quantitative concentration of aliphatic hydroxyl groups determined in the pulp lignin effluents that were obtained from the O, OO, and mini-O trials of the LK and HK pulps.

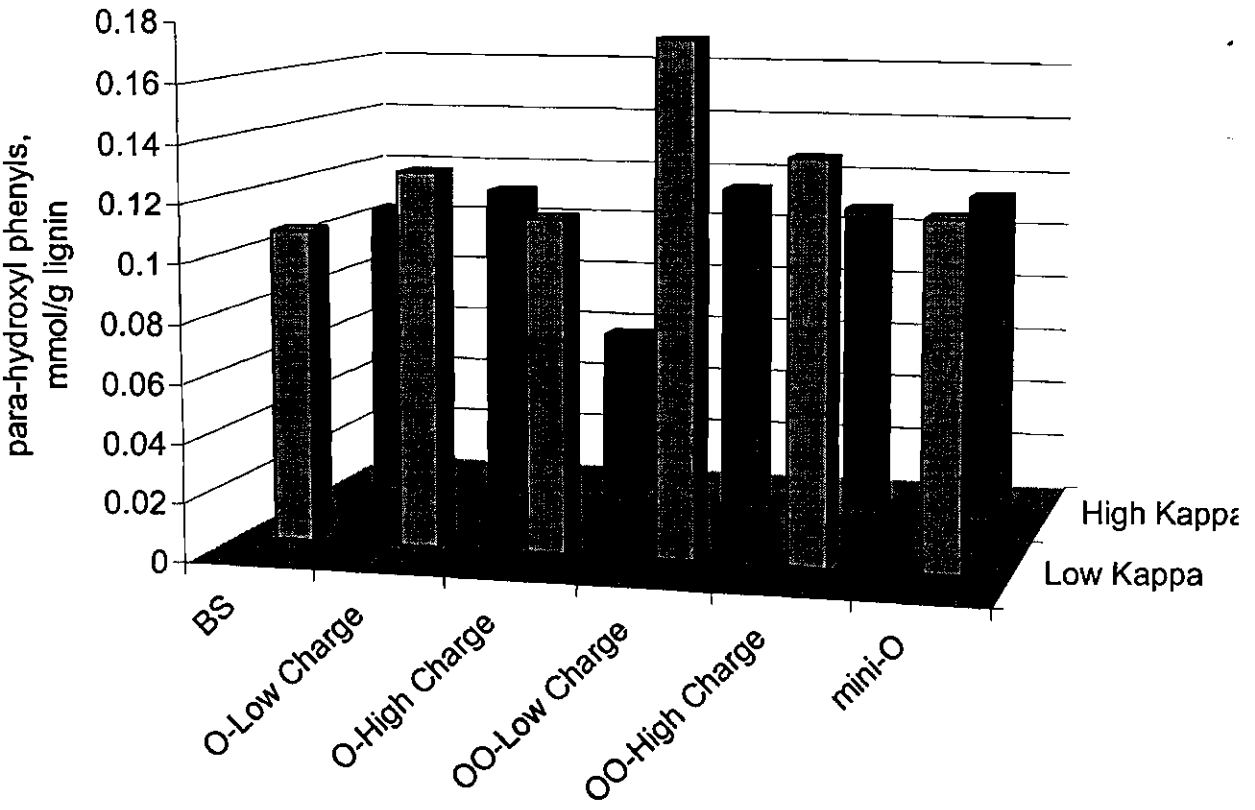


Figure 11. The quantitative concentration of the para-hydroxy phenyl groups (138.3 – 137.0 ppms) determined in the pulp effluents that were obtained from the O, OO, and mini-O trials of the LK and HK pulps.